A crossed molecular beam investigation of the reaction Cl + propane $\rightarrow$ HCl + C_3H_7 using VUV synchrotron radiation as a product probe.

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Radical abstraction of primary or secondary H atoms in hydrocarbons represents a crucial aspect of the dynamics of these reactions, important for developing a predictive understanding of combustion systems. We have used the crossed molecular beam technique to study the hydrogen atom abstraction from propane by atomic chlorine over a wide range of collision energies. The experiments were carried out using endstation 1 on the Chemical Dynamics Beamline at the ALS. The use of soft ionization via tunable undulator radiation has allowed for direct measurements of the radical fragment in these reactions for the first time. We have measured laboratory TOF spectra and angular distributions for Ecoll = 8.0, 11.5, and 31.6 kcal/mol. Center-of-mass flux maps were generated from the measured laboratory distributions.

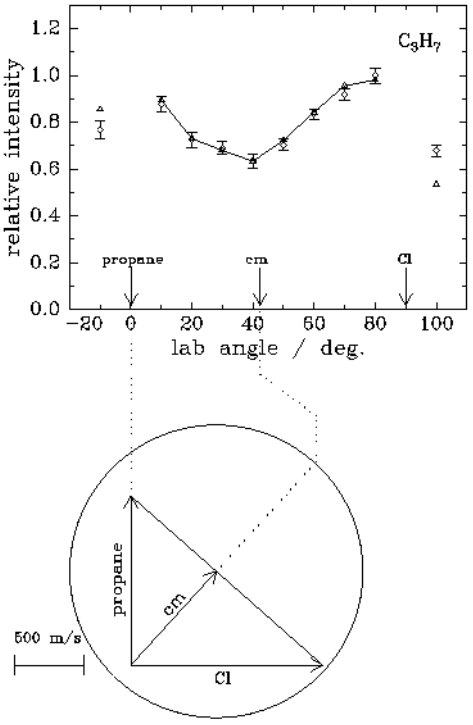

Figure 1. Laboratory angular distribution and Newton diagram for propyl radical product from the crossed beam reaction of Cl+propane at a collision energy of 8.0 kcal/mol.

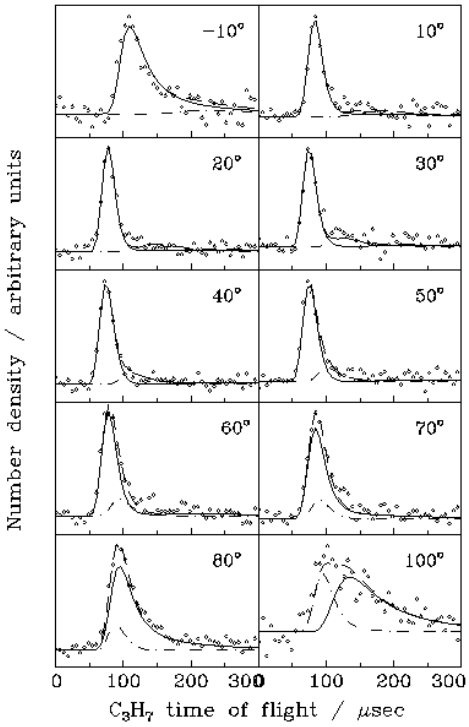

Figure 2. Time-of-flight data at the indicated lab scattering angle for propyl radical product from crossed-beam reaction of Cl+propane at 8 kcal/mol collision energy.

The experimental angular distribution (Fig. 1) and time-of-flight spectra (Fig 2) for this reaction at a collision energy of 8.0 kcal/mol are shown in Figs. 1 and 2. From the distributions in Figs. 1 and 2, we derive the center-of-mass translat onal energy distributions shown in Fig. 3. The results demonstrate two distinct reaction mechanisms that depend on the impact parameter of the reactive collision. Large impact parameter collisions proceed via a stripping mechanism resulting in forward scattered products with very little momentum change in going from reactant to product.

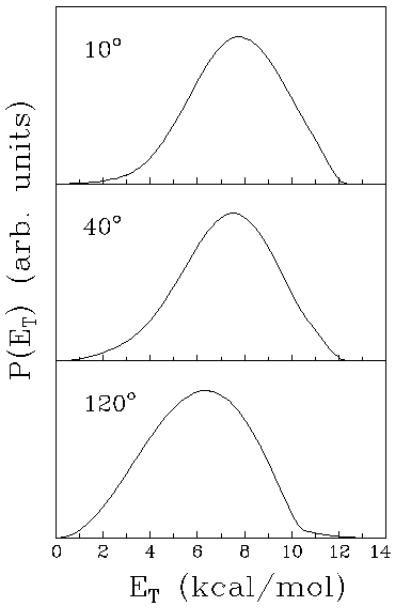

Figure 3. Translational energy distributions inferred from the simulations for the indicated center of mass scattering angles. The results show near stripping behavior for the forward scattered product, implying long-range collisions with little momentum transfer. The backscattered product shows lower translational energy release, implying a 'close collision' and greater momentum transfer.

The stripping reactions are most likely dominated by abstraction of secondary hydrogen atoms. Smaller impact parameter collisions lead to direct reactions with an impulsive recoil and are consistent with a preference for collinear transition state geometry, -C-H-Cl. Direct collision via this collinear configuration is necessary to overcome the entrance barrier for abstraction of primary H atoms. At higher collision energy, the effect of this barrier becomes less important, leaving the ratio of primary to secondary hydrogen abstraction to be dictated by simple statistics. These experiments reveal distinct dynamics and internal energy distributions for the two different radical products resulting from secondary or primary H atom abstraction from propane.

REFERENCES

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